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Residual stresses and density gradient in injection molded starch/synthetic polymer blends

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Abstract

Residual stress distribution in injection molded starch/synthetic polymer blends was evaluated using the layer removal technique. The synthetic polymers in the blend were either polybutylene succinate (PBS) or polycaprolactone (PCL). The starch content ranged from 0 to 70% by weight in the PBS blend and was held constant at 70% in the PCL blend. The effects of various molding conditions, aging and starch content were investigated. The residual stress profiles were found to be parabolic in nature with surface compressive stresses and interior tensile stresses. Increasing the injection pressure and mold temperature decreased the tensile stresses but had no significant effect on the surface compressive stresses. Decreasing the packing pressure produced a significant decrease in the magnitude of residual stresses. Varying melt temperature and packing time did not significantly affect the residual stress distribution for the range of values investigated. The residual stresses relaxed with time, decreasing over a period of 57 days. The magnitude of residual stresses increased as the starch content in the PBS blends was varied from 0 to 70%. Density gradient measurements were made in a 70% starch/PBS blend. The density was found to be higher in the interior than at the surface with a steep gradient close to the surface. Varying the molding conditions had a complex effect on the average density and the density distribution. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Starch/synthetic polymer blends; Residual stress distribution; Starch content

1. Introduction

Development of biodegradable polymeric materials has been of interest in recent years because of its impact on the environment. However, there is a lack of wide-scale adoption of these materials by industry largely due to the high cost of synthetic biodegradable polymers. In addition, adoption of any new material by the manufacturing industry requires that it be well characterized in terms of its behavior under various processing, manufacturing and usage conditions. One of the most widely used and well-studied polymer processing methods in the plastics industry is injection molding. It is characterized by low cost, high production rates and dimensional accuracy of the product. During the process, molten polymer is injected into a mold cavity at high speeds and then allowed to cool and solidify followed by ejection of the part from the mold. Residual stresses are introduced into the part as a result of non-homogeneous and non-isothermal filling, packing and cooling of the hot melt in the mold cavity. Thus, the injection molding process provides a logical testing environment for performance characterization of materials.

In order to mitigate the impact of the high cost of synthetic biodegradable polymers, starch has generally been added to make a polyblend. Starch also increases the modulus and reduces the cycle time of these blends. Research has been conducted over the past several years on the suitability of using starch/synthetic polymer blends for application in commercial products. Mani et al. [1] have presented a detailed review of the recent developments in biodegradable plastics and the use of starch in them. Improvements in the properties of starch/synthetic polymer blends and the process used for making them have made the prospect of their commercial production and use a reality.

In this study, residual stress and density profiles in injection molded starch/synthetic polymer blends have been evaluated with the ultimate objective of characterizing material behavior for use in product design. Residual stresses introduced into injection molded parts arise from a combination of flow and thermal (or cooling) stresses. Flow stresses are a result of shear, normal and extensional stresses generated during filling and packing of the mold and are tensile in nature. Thermal stresses arise due to non-isothermal cooling of the part and display a parabolic

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Table 1
Properties of polyesters used in the starch/polyester blends (manufacturers data)

Property	PBS	PCL-767	PCL-787
Glass transition (°C)	−32	−60	−60
Melting point (°C)	115	60	60
MFI (g/10 min)	25 [190°C/2.16 kg]	1.9 [80°C/303.2 KPa]	1.0 [125°C/303.2 KPa]

profile across the part thickness with compressive stresses at the surface and tensile stresses towards the center. The non-isothermal cooling associated with the development of residual stresses also gives rise to volumetric effects that create a density gradient across the part thickness. The residual stress and density profiles together have a significant influence on the mechanical properties and quality of injection molded parts.

Several techniques have been developed over the years for estimation of residual stresses in injection molded parts. A review of these techniques can be found in Ref. [2]. The layer removal technique of Treuting and Read [3] was used to estimate the residual stress distribution in this study. Some recent developments in measurement techniques include the use of finite width slots [4] and embedded fiber optic sensors [5].

The objective of this study was to evaluate the effect of starch content and molding parameters on the gap-wise residual stress and density distributions in injection molded starch/synthetic polymer blends. The synthetic polymers used were polyesters and the blends contained 5% w/w of maleic anhydride functionalized polyesters. These maleated polyesters behave as compatibilizers and promote adhesion between the starch and polyester phases, which are otherwise incompatible. This is achieved by a reaction between the grafted anhydride group in the functionalized polyester and the hydroxyl group in the starch molecules, producing a chemical bond. The result is a significant improvement in mechanical strength of the blend when compared to just a physical mixture of starch and synthetic polymer [6].

2. Experimental

2.1. Materials

The starch used was Midsol 1, a premium wheat starch obtained from Midwest Grain Products, Inc., Atchison, KS. The synthetic polymers used were semi-crystalline polyesters. Polybutylene succinate (PBS, trade name Bionolle, Grade 1020) was obtained from Showa Highpolymer Co., Ltd., Tokyo, Japan, and two grades of polycaprolactone (PCL, Grade 767 and Grade 787) were obtained from Union Carbide Corporation, Danbury, CT. In starch/PCL blends, PCL-767 was the pure synthetic polymer component, while PCL-787 was used as the functionalized component. The properties of the respective polyesters are included in Table 1.

2.2. Functionalized polyester

Functionalization of the polyester was achieved by grafting maleic anhydride (MA) onto the respective polyester in a reactive extrusion process using dicumyl peroxide (DCP) as initiator. This was carried out in a laboratory-scale corotating, twin-screw extruder (Rheomex TW-100, Haake Scientific Instruments, Paramus, NJ). The percentage grafting and intrinsic viscosity of the grafted polyester was estimated to check against degradation. The details can be found elsewhere [7,8].

2.3. Blending

Compositions containing 0, 10, 30, 50 and 70% starch by weight were blended in a HAAKE co-rotating, twin screw extruder. The blend composition and the processing conditions are summarized in Tables 2 and 3, respectively. The designation assigned in Table 2 has been used henceforth to refer to each blend. The extrudate was allowed to cool before being ground and stored in sealed polyethylene bags with Drierite®, and then used for injection molding samples.

Table 2
Composition of starch/synthetic polymer blends used in the experiments

Blend designation	Starch content (w/w%)	Polyester content (w/w%)	Functionalized polyester content (w/w%)
B70	70	25 (PBS)	5 (PBS-MA)
B50	50	45 (PBS)	5 (PBS-MA)
B30	30	65 (PBS)	5 (PBS-MA)
B10	10	85 (PBS)	5 (PBS-MA)
B00	0	100 (PBS)	0
C70	70	25 (PCL 767)	5 (PCL 787-MA)

Table 3
Processing conditions used during blending

Parameter	Starch/PBS blends	Starch/PCL blends
Barrel temperature[a] (°C)		
Zone 1 (Feed)	120	90
Zone 2	130	120
Zone 3	130	120
Zone 4 (Die)	130	90
Screw speed (r.p.m.)	60	60
Torque (N-m)	14–20	14–20

[a] From feed zone to nozzle temperature, respectively.

2.4. Injection molding

The blends were injection molded into rectangular bars in a BÖY 50 ton machine. The mold used had an end-gated, rectangular cavity of dimensions $152.5 \times 39.3 \times 10.0\ \mathrm{mm}^3$. After the molding process had reached steady state (constant mold and barrel temperatures, injection speed variation <5 mm/s for three consecutive parts), samples were collected. The process conditions used are summarized in Table 4. The conditions were selected based on part appearance and machine limitations. For each blend composition, a total of 26 specimens were molded sequentially for each blend or molding condition evaluated. For estimation of Young's modulus and Poisson's ratio, ASTM Type II dog-bone specimens were molded under the same conditions as in Table 4.

2.5. Layer removal

Rectangular specimens, $55 \times 6.4\ \mathrm{mm}^2$, were removed along the longitudinal axis of the molded bars at a distance of 35 mm from the gate. These specimens had the same thickness as the molded bars. They also did not exhibit any curvature in the transverse direction implying they were at equilibrium. A BENGAL abrasive water-jet machine (Flow International Corp., Kent, WA) was used to remove incremental layers of material. This method of layer removal was chosen, as it is known to be a stress-free operation [9]. In addition, a conventional rotating end-mill was also used for comparison purpose. The effect of the two-layer removal method on the residual stress was verified by comparing the stress profiles obtained in both annealed and injection molded specimens. This process gave an estimation of the stresses induced due to the layer removal operation as annealing is expected to relieve all internal stresses in the specimens. The abrasive water-jet was the method of choice based on the results obtained.

Table 4
Reference molding conditions and the parameters that were varied for evaluating their effect on the residual stress and density distributions

Parameter	Reference value	Varied value
Barrel temperature[a] (°C)	115, 130, 145, 145[b] 110, 115, 120, 120[c]	125, 140, 155, 155[b]
Mold temperature (°C)	20	45
Injection pressure (MPa)	11.1	16.2
Packing pressure (MPa)	11.1	6.1
Packing time (s)	20	5

[a] From feed zone to nozzle temperature, respectively.
[b] Starch/PBS blends.
[c] Starch/PCL blends.

Layer removal operations were done in increments of 0.4 mm. After layer removal, the sample was dried by gently dabbing with paper tissue followed by a blast of compressed air for about 45 s. This made the sample dry to the feel. Drying was accomplished within 1 min of layer removal in order to minimize water absorption. Curvature was measured within 2 min after this using a MicroVal® co-ordinate measuring machine (Brown and Sharpe Manufacturing Co., North Kingstown, RI). Co-ordinates of the machined surface were recorded at the mid-plane along the length of the specimen using a 2.5 mm diameter probe. The trigger force for the probe was found to be 7.9×10^{-2} N ^ 6.25%. A simple calculation showed that the deformation caused by this force was negligible.

Curvature, c, of a curve represented as $y = f(x)$ is given by:

$$c = \frac{\dfrac{d^2y}{dx^2}}{\left[1 + \left(\dfrac{dy}{dx}\right)^2\right]^{3/2}} \tag{1}$$

This could be approximated by d^2y/dx^2 over the range of values concerned. Treuting and Read [2] give the residual stress distribution as

$$\sigma_x(z_1) = \frac{-E}{6(1-\nu^2)}\left\{(z_0 + z_1)^2\left[\frac{d\varphi_x(z_1)}{dz_1}\right] + 4(z_0 + z_1) \times [\varphi_x(z_1)] - 2\int_{z_1}^{z_0} \varphi_x(z)\, dz\right\} \tag{2}$$

Here, E is the Young's modulus, ν is Poisson's ratio, z_0 is the half thickness of the specimen, z_1 is the distance from the center to the surface of the specimen after layer removal, φ_x is the curvature in the x-direction. This is a special form of the general case for biaxial stress distribution and assumes that curvature in the y-direction is negligible. This assumption was made based on the low width to thickness ratio (about 0.65) of the specimen. Other assumptions for the calculation procedure are that there is no variation in stress distribution over the length of the specimen, the material is isotropic, elastic, linear in pure bending and that no stresses are introduced during the layer removal procedure. For polymeric materials, it is also necessary to ensure that there is no stress relaxation or creep during the time frame of layer removal and curvature measurement. From the fit to the ϑ_x vs. z_1 plot, the stress distribution was calculated using

Eq. (2). For comparing the results to that reported in literature previously, an estimation of the error was done by calculating the average stress per unit width as:

$$(\sigma_x)_{\text{avg}} = \frac{\int_0^{z_0} \sigma_x(z)\,\mathrm{dz}}{\int_0^{z_0} \mathrm{dz}} \tag{3}$$

Since the numerator is actually the net force acting per unit width, equilibrium requires it to be zero. Thus, a non-zero value was considered as a representation of the error. This was then expressed as a percentage of the maximum magnitude of measured stress. The deviation of the stress distribution from equilibrium was also estimated as a non-dimensional expression:

$$(\sigma_x)_{\text{dev}} = \frac{\int_0^{z_0} \sigma_x(z)\,\mathrm{dz}}{\int_0^{z_0} |\sigma_x(z)|\,\mathrm{dz}} \tag{4}$$

2.6. Annealing

Annealed specimens of B70 were used for estimation of stresses introduced due to the machining process used for layer removal. Annealing was done by holding the molded bars at 90°C for 48 h followed by cooling to room temperature over 24 h. This temperature was well above the glass transition of the synthetic polymer and close to its melting point. The PBS grade used had a glass transition temperature of −32°C and a melting point of 115°C. Starch melts at temperatures in the range of 120–130°C. Thus, all internal stresses are expected to have been relieved by this annealing process.

2.7. Young's modulus

Young's modulus values are required for computing the residual stress magnitude using Eq. (2). Specimens of all blends were molded under reference conditions. B70 specimens were molded under the various conditions listed in Table 4.

The specimen for Young's modulus measurements were stored in sealed polyethylene bags to be used for evaluation at 14 h after molding, which was the time at which layer removal was done for residual stress measurements. To evaluate the effect of aging, B70 samples were stored in a sealed polyethylene bag inside an oven at a temperature of 28°C. 10 specimens were removed at 0.5, 7, 27 and 57 days after molding and tested for Young's modulus.

2.8. Poisson's ratio

Poisson's ratio was evaluated from the longitudinal and transverse strains in uniaxial loading. Annealed ASTM D638-Type II specimens were used. Transverse strain was measured using a bonded strain gage (EA-13-062AQ-350, Measurements Group Inc., Raleigh, NC.) in a half-bridge circuit. Longitudinal strain was measured using an extensometer. Using strain gages for measuring both transverse and longitudinal strains would have required the gages to be placed next to each other on the specimen. Using just one strain gage minimized any heat generation and reinforcement effects, both of which are significant concerns for a thermoplastic material. The loads applied were 10, 20, 30 and 40 N. Measurements were made on specimens with varying starch contents molded at the reference conditions only.

2.9. Density gradient measurements

Rectangular bars of the same dimensions as those used for residual stress measurements were injection molded. Measurements were conducted on B70 specimens molded under the different conditions shown in Table 4. $2 \times 5\ \text{mm}^2$ samples were removed from the center of the bars at a distance of 60 mm from the gate. A microtome was used to remove 20 μm slices from the surface to the center. Density measurements were made in a density gradient column at 22°C. Toluene (density 0.86 g/cm^3) and carbon tetrachloride (density 1.59 g/cm^3) were the two liquids used in the column.

3. Results and discussion

A total of 26 specimens were molded sequentially for each blend or molding condition evaluated. The molded samples were numbered sequentially but in pairs to form 2 sets of 13 samples. This was done to serve two purposes. First, the two sets of specimens provided a duplication of experimental data. Second, it was not possible to remove uniform successive layers from the same specimen as a curvature was induced after removal of the very first layer. It was verified that the fixture used prevented the specimen from curving during the layer removal process. But the nature of the abrasive water-jet cutting process prevented the use of any restraints that would hold the specimen flat after removal of the first layer and allow removal of subsequent layers from the same specimen. Thus, it was necessary to remove layers of increasing thickness from separate specimens molded at the same time and under the same conditions. It was assumed that the residual stress distribution was symmetrical across the half-thickness of the molded bars. Therefore, layer removal from the surface to only the half-thickness was considered sufficient. Since the bar thickness was about 9.5–9.8 mm, removal of twelve layers of 0.4 mm thickness provided data points almost up to the mid-plane. A 13th specimen was always molded as a spare to be used if cavities were found in the specimens, which did occur occasionally. Thus, during the final layer removal process, out of the 26 molded bars, only two sets of 12 specimens, i.e. a total of 24, were used to obtain data points.

Table 5
Young's modulus, UTS/yield strength and Poisson's ratio values for the blends. Only blends B00 and B10 showed a yield strength

Blend	Young's modulus, E (MPa)	Ultimate tensile strength (UTS)/Yield strength (σ_y) (MPa)	Poisson's ratio, ν
B70	2163	35.1	0.479
B50	1435	33.9	0.449
B30	837	33.1	0.422
B10	609	34.3	0.419
B00	469	32.4	0.383
C70	1262	18.4	0.479 (assumed)

The average time for injection molding of 26 rectangular bars was about 75 min which was about the same time it took to remove layers from 24 of them in the same sequence in which they were molded. This ensured that layer removal was performed on the specimens at a constant time after injection molding. As explained by Isayev and Crouthamel [10], this prevented any discrepancy in the data due to relaxation of stresses.

In order to evaluate repeatability of the method, three sets of 26 samples were molded under reference conditions using B70. The layer removal procedure was performed on them. As mentioned earlier, each set provided data for two stress distribution profiles and hence a total of six stress distribution profiles were obtained. This data was used to create a mean stress distribution profile along with the 95% confidence limits, which is henceforth referred to as the reference curve. The effect of varying a molding parameter could thus be evaluated by comparing the residual stress profile to the reference curve.

3.1. Material properties

Young's modulus, UTS and Poisson's ratio of all blends are shown in Table 5. The general trend indicates that all three property values increase in magnitude with increasing starch content. The Young's modulus of the 70% starch/PBS blend was 4.6 times that of pure PBS, while its UTS was 1.08 times that of the yield strength of pure PBS. The Poisson's ratio of a 70% starch/PBS blend was found to be 0.479. A comparison based on a one-tailed t-test for two samples with unequal variances indicated that there was no significant difference at the 95% confidence level in the UTS and Poisson's ratio values for the PBS blends with 10% and 30% starch content. Both yield strength and Poisson's ratio showed a jump when just 10% starch is added to the synthetic polymer. With subsequent increase in starch content from 30 to 70%, the increase in yield strength and Poisson's ratio was more gradual. The Young's modulus showed a gradual increase with increasing starch content. There was no "jump" with the addition of 10% starch and in fact the increase in Young's modulus was steeper when the starch content increased from 30 to 70%, than when it increased from 0 to 10%. The 70 starch/PCL blend had a lower Young's modulus and UTS, in keeping with reduced mechanical properties of PCL.

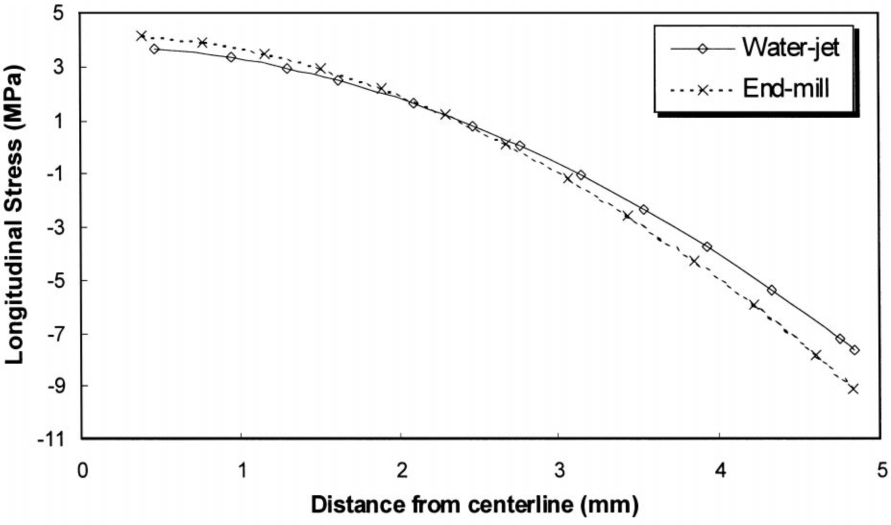

Fig. 1. Residual stress distribution obtained by two methods of layer removal—an abrasive water-jet and an end mill. Injection molded B70 samples were used (not annealed).

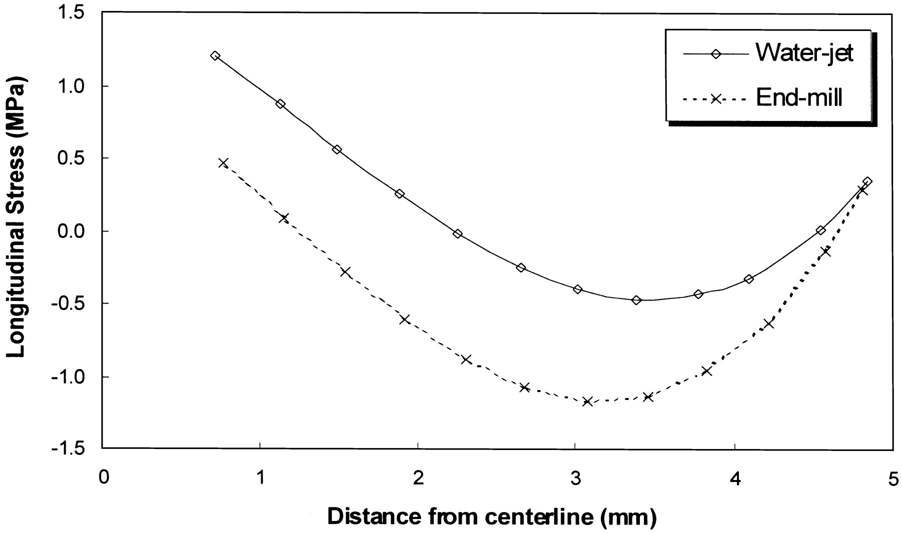

Fig. 2. Residual stress distribution obtained by two methods of layer removal—an abrasive water-jet and an end mill. Annealed B70 specimens were used.

3.2. Residual stress measurements

3.2.1. Estimation of curvature

The procedure for calculating the stress distribution profile was applied as outlined in the previous section. The curvature profile for each specimen was plotted and fitted with a second order polynomial by the least squares method. The fit was found to be reasonably good to excellent for most of the curvature profiles, with an R^2 value ranging from 0.8 to 0.99. The lower values of R^2 were usually observed for the initial layer removals close to the surface. In this region, the curvature values are extremely small. Thus, the measurement errors are larger. Moreover, using higher order polynomials did not improve the fits to measured curvature profile data. The general trend showed that with increasing specimen curvature the R^2 value increased before reaching a plateau. A simple analysis showed that over the range of values concerned, the curvature calculated by Eq. (1) could be approximated by just d^2y/dx^2, as the denominator deviated very little from unity. The maximum deviation of the curvature from the mean value was about 2%. Thus, a second order polynomial almost had a constant curvature over the range of dimensions concerned.

Table 6
Cutting parameters used by the abrasive water-jet and milling machines for comparison purposes

Abrasive water-jet cutting		Milling machine	
Water pressure	275.6 MPa	RPM	3000
Cutting speed	3.81 mm/s	Feed rate	3.81 mm/s
Orifice opening	0.33 mm	Cutter diameter	12.7 mm
Abrasive	80 mesh		
Mixing nozzle diameter	1.016 mm		

3.2.2. Comparison of different layer removal techniques

The results of the comparison between using a conventional end mill and an abrasive water jet for performing layer removal is shown in Figs. 1 and 2. The corresponding machining parameters are specified in Table 6. The stress distribution in Fig. 1 was obtained using injection molded specimens at 14 h after molding and those in Fig. 2 were obtained for annealed samples. The peak compressive and tensile stresses obtained and the area under the curve over half the thickness are reported in Table 7.

For the molded samples, the stress distribution profile was parabolic in nature with a compressive stress at the surface and tensile stresses in the interior. The magnitude of stresses obtained using the end-mill were higher than that obtained using the abrasive water-jet. Also, the area under the curve showed a larger imbalance for the end-milled samples. The stress profiles were obtained with a linear fit to the φ_x vs. z_1 data. For the annealed samples the magnitude of stresses was much lower and the profile obtained was not parabolic. The φ_x vs. z_1 data required a quadratic fit.

An estimation of error produced by the layer removal technique was done by calculating the average stress per unit width using Eq. (3). In the molded samples, the average stress was about 0.51% of the maximum stress for abrasive water-jet milling and about 2.42% of the maximum stress for conventional end-milling. In annealed samples, the corresponding values were 22.23% and 32.52%, respectively. It was noted that compressive stresses dominated the stress profile for the end-mill process and tensile stresses dominated for the abrasive water-jet case. Also, in both injection molded and annealed samples, the imbalance in the area under the curve was higher when an end-mill was used for layer removal.

To estimate the effect of creep, curvature values were measured immediately after layer removal (within 3 min) and at 50 h after layer removal. The curvature of the

Table 7
Data for residual stress values obtained by layer removal using an abrasive water-jet and a conventional end-mill for injection molded and annealed samples

	Method of layer removal	Abrasive water-jet	Conventional end-mill
Injection molded	Max. compressive stress (MPa)	−7.64	−9.08
	Max. tensile stress (MPa)	3.66	4.17
	Average stress over half-thickness (MPa)	−0.039	0.22
	Non-dimensional deviation $(\sigma_x)_{dev}$	0.003	0.013
Annealed	Max. compressive stress (MPa)	−0.47	−1.16
	Max. tensile stress (MPa)	1.21	0.47
	Average stress over half-thickness (MPa)	0.268	0.377
	Non-dimensional deviation $(\sigma_x)_{dev}$	0.099	0.194

specimens increased over this period of time. This increase ranged from about 21 to 276%. The magnitude of residual stresses calculated with the curvature measured at 50 h after layer removal was also found to be higher. The surface compressive stress was higher by about 2 MPa and the tensile stress at the center was higher by about 1 MPa. Hence, it was deemed necessary to measure curvature as soon as possible after layer removal to prevent skewed results. This is consistent with the observations of Isayev and Crouthamel [10].

Exposure to water for 2 min (the approximate time required to accomplish the removal of the layer using the water jet) was found to have no significant effect on either Young's modulus or ultimate tensile strength for B70. Water absorption in the samples was found to be negligible (<0.15%) for a 2 min immersion.

3.2.3. Repeatability

The six sets of data obtained from the repeatability experiments were used to generate the reference curve which is shown in Figs. 3–5. The 95% confidence envelope is also shown via the dashed lines. The standard deviation for the mean reference curve is shown in Fig. 6. The data shows a larger magnitude of variation close to the surface which is reflected in the higher standard deviation (Fig. 6) and wider 95% confidence envelope (Fig. 3) close to the surface. This is possibly due to the low value of curvature produced by layer removal near the surface and the associated larger error in fitting a quadratic polynomial to estimate this curvature.

3.2.4. Effect of process conditions

The effect of various molding conditions on the residual stress distribution profile across the specimen thickness is shown in Figs. 3–5. All stress distribution profiles were found to be parabolic in nature. This was a direct result from a linear fit to the plot of curvature vs. distance from centerline. A statistical analysis software package [11], was

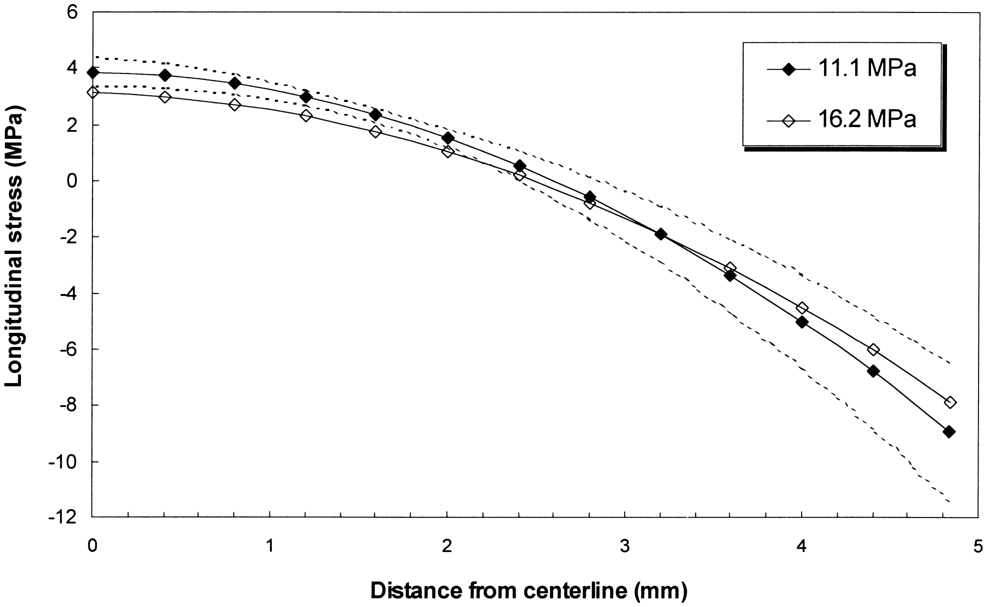

Fig. 3. Effect of injection pressure on the residual stress distribution for B70. The distribution for injection pressure 11.1 MPa is the reference curve and the dashed lines represent the 95% confidence envelope obtained form the repeatability experiments.

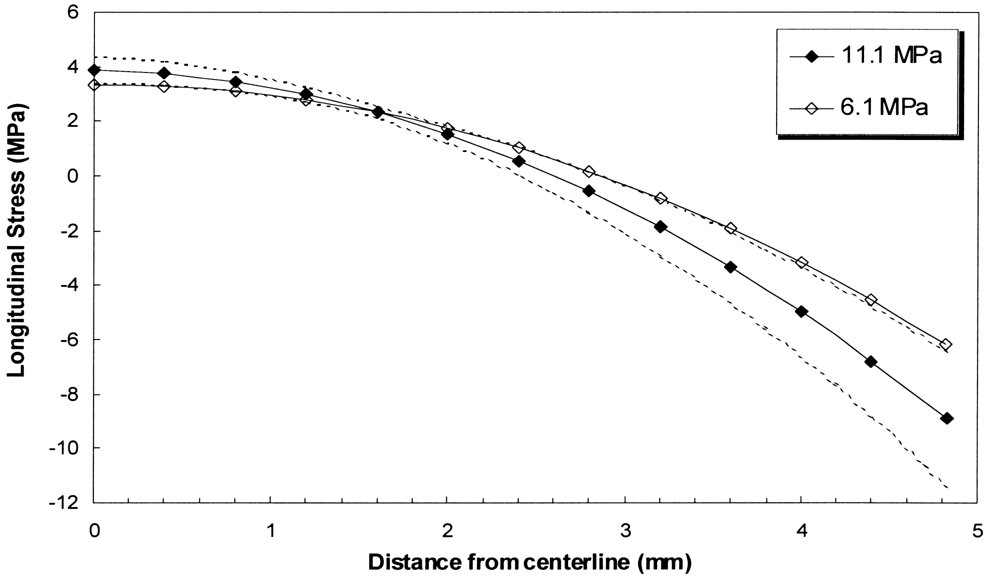

Fig. 4. Effect of packing pressure on the residual stress distribution for B70. The curve for a packing pressure of 11.1 MPa is the reference curve and the dashed lines represent the 95% confidence envelope obtained from the repeatability experiments.

used to evaluate the best fit to the plot by a two-tailed t-test. A linear fit to the data was found to be good in all cases except for the annealed specimens used in comparing the two methods of layer removal. In that case, a quadratic fit was used, which resulted in a non-parabolic stress distribution profile (Fig. 2). Increasing the injection pressure from 11.1 to 16.2 MPa decreased the magnitude of both surface compressive stresses and interior tensile stresses (Fig. 3). But the decrease in surface compressive stresses was not found to be significant at the 95% confidence level. The decrease could be attributed to shear heating caused by higher injection speeds at the higher injection pressure. This would result in a higher temperature within the mold leading to greater stress relaxation. Siegmann et al. [12] found that surface stresses initially increased with increasing injection pressure, reached a peak, and then decreased. They varied injection pressure in the range of 6.1 to 13.2 MPa. Kubat and Rigdahl [13] have stated that internal stresses in LDPE and HDPE changed from compressive to tensile when injection pressure was increased from 100 to 450 MPa. But their use of the stress relaxation technique for making measurements does cast some doubt about the interpretation of their data. The injection rate (or speed) has been shown to have a significant effect in studies by Siegmann et

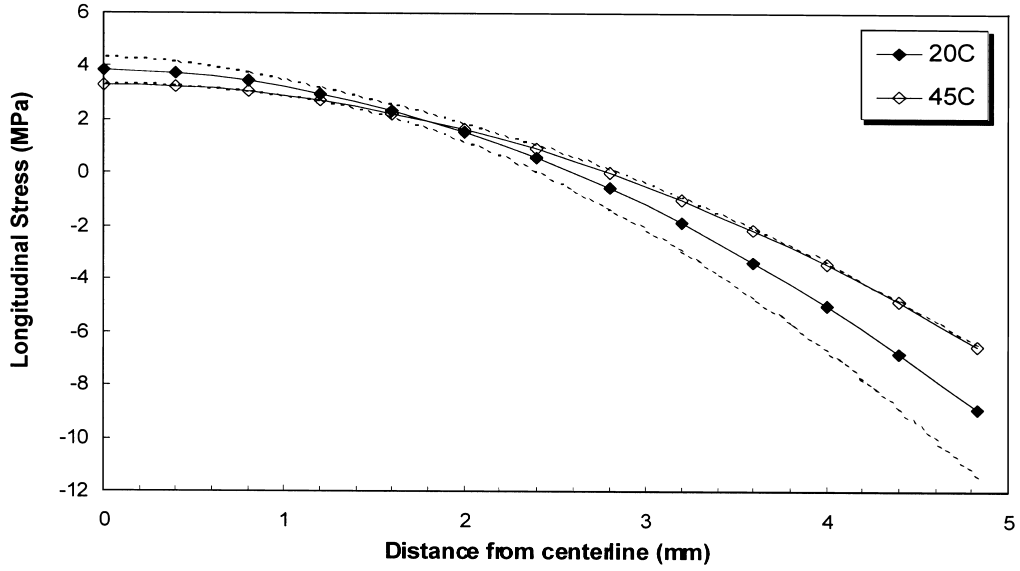

Fig. 5. Effect of mold temperature on the residual stress distribution for B70. The curve for mold temperature of 0°C is the reference curve and the dashed lines represent the 95% confidence envelope obtained form the repeatability experiments.

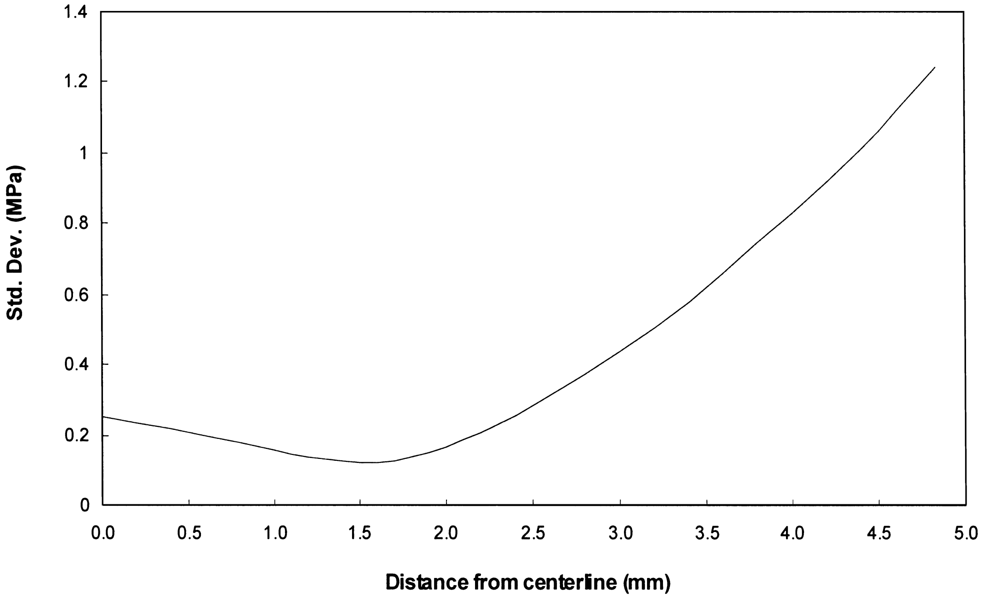

Fig. 6. The standard deviation and RMS error associated with the mean reference curve for B70 shown in Figs. 4–6.

al. [12] and Isayev and Crouthamel [10]. They found the surface compressive stresses to decrease with decreasing injection rate and even become tensile at very low rates.

Reducing the packing pressure decreased the magnitude of both surface and interior stresses as shown in Fig. 4. But packing time did not have a significant effect at the 95% confidence level over the range considered. This indicates that the gate is almost frozen at 5 s after filling.

A 25°C increase in mold temperature decreased both surface compressive stresses and interior tensile stresses (Fig. 5). But, only the decrease in interior tensile stresses is significant at the 95% confidence level (for distance from centerline <1 mm). This decrease in stress magnitude is readily explained by the fact that a higher mold temperature decreases the cooling rate of the part in the cavity, thereby allowing more time for stresses to relax. A similar explanation may be found in the investigations of Saffel and Windle [14], and Siegmann et al. [15]. This influence appears to be greater in the interior of the part than at the surface for a 25°C rise in mold temperature. Investigations by Russel and Beaumont [16], Siegmann et al. [15] and Isayev and Crouthamel [10] indicate a similar effect with surface stresses decreasing with increasing mold temperature.

Increasing the nozzle temperature by 10°C, from 145 to

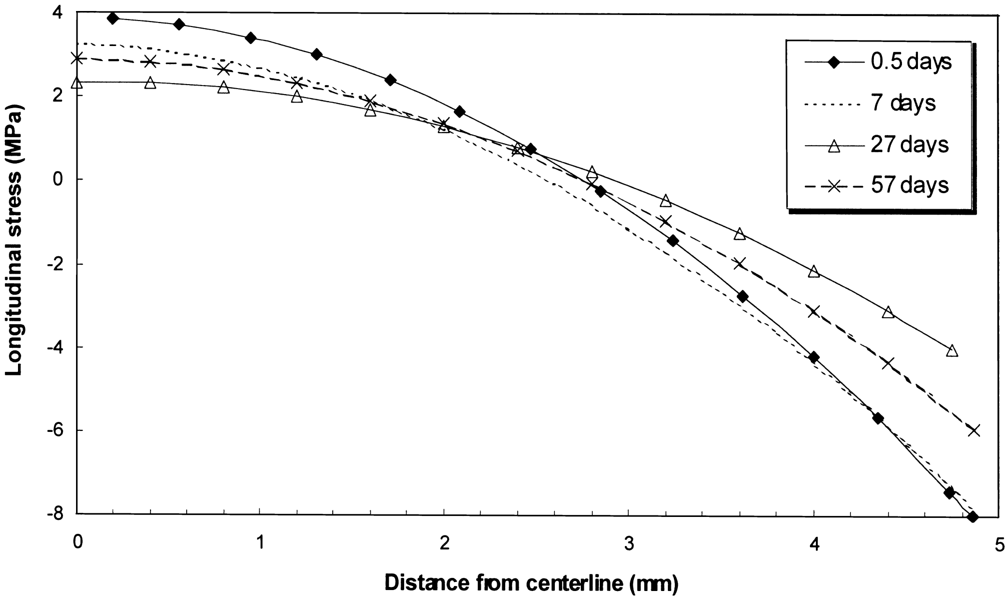

Fig. 7. Effect of aging on the residual stress distribution for B70. Injection molding was done under reference conditions.

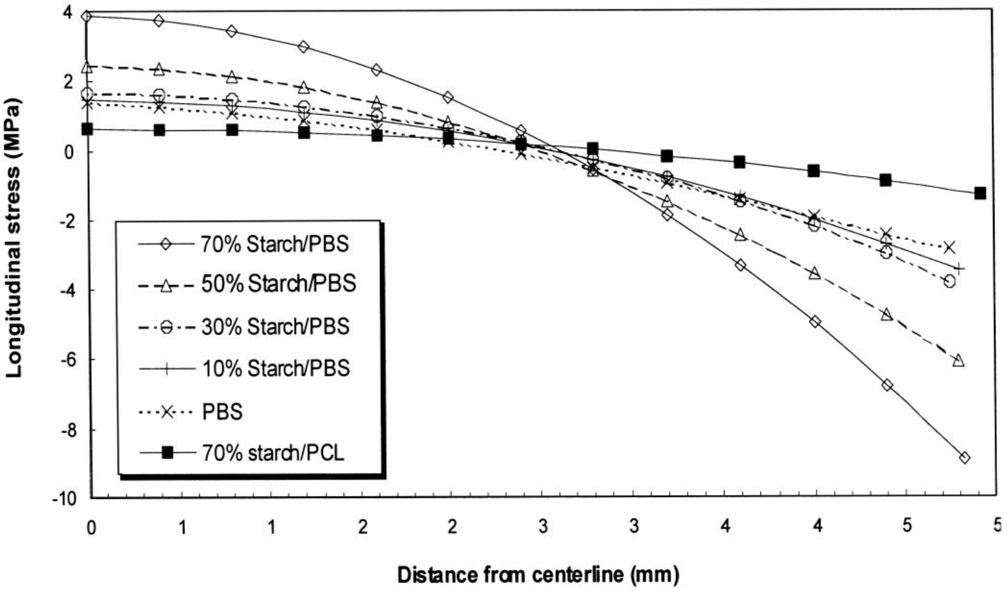

Fig. 8. Effect of blend composition on the residual stress distribution for starch/polyester blends. Injection molding was done under reference conditions.

155°C, had no effect on the residual stress distribution. The investigations by Siegmann et al. [15] indicate a decrease in surface compressive stresses when melt temperature was increased by 40–55°C, for PA and PSF specimens. On the other hand, Isayev and Crouthamel [10] report that increasing the melt temperature decreased the surface compressive stresses in molded PS strips. This was explained by the dominance of tensile flow stresses at lower melt temperatures.

The magnitude of residual stresses was found to decrease with time over a period of 57 days as shown in Fig. 7. Thus, stress relaxation did occur and justified the need to conduct the layer removal process at the same time after molding for all samples in order to maintain a basis for comparison. The measured Young's modulus and UTS did not show a significant change over the same period of time.

3.2.5. Effect of starch content

Increasing the starch content was found to increase the magnitude of residual stresses. This is shown in Fig. 8. This could occur due to the corresponding increase in Young's modulus and Poisson's ratio with increasing starch content. In order to investigate this, non-dimensional stress vs. z_1 was plotted for different starch contents as shown in Fig. 9. The

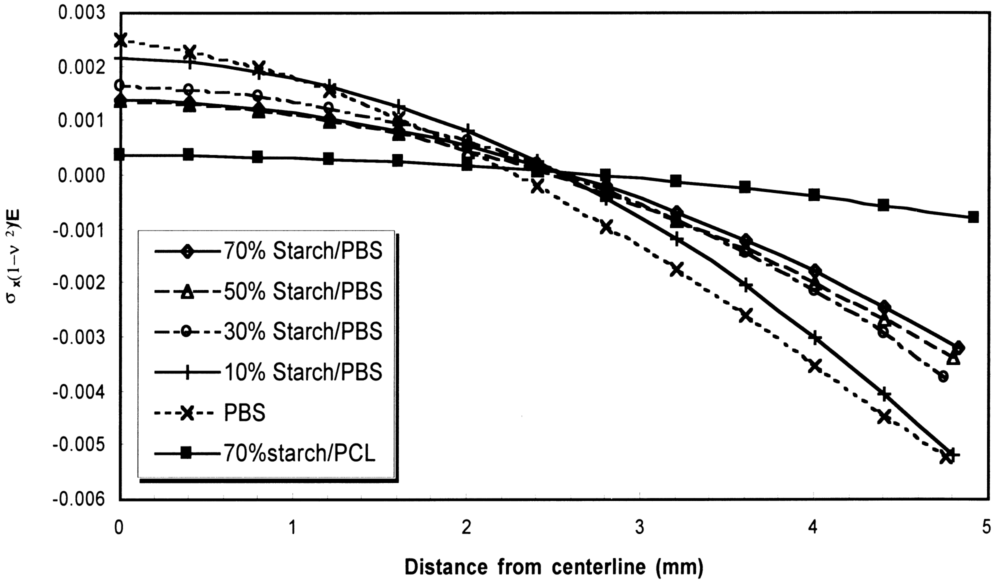

Fig. 9. Non-dimensional plot showing the effect of starch content on the residual stress distribution for starch/polyester blends. Injection molding was done under reference conditions.

Table 8
Average stress values obtained from the experimentally determined residual stress profiles

Experiment	Specimen	Average stress (MPa)	Average stress (% of max. stress)	Non-dimensional deviation $(\sigma_x)_{\text{dev}}$
Effect of molding conditions (70% starch/PBS)	Reference	−0.464	5.2	0.15
	Injection pressure 16.2 MPa	−0.681	8.6	0.25
	Packing pressure 6.1 MPa	0.197	3.2	0.08
	Packing time 5 s	0.041	0.7	0.02
	Mold temperature 45°C	0.043	0.7	0.02
	Nozzle temperature 155° C	−0.482	5.5	0.15
Effect of starch content	50% starch/PBS	−0.472	7.8	0.22
	30% starch/PBS	−0.167	4.4	0.12
	10% starch/PBS	−0.223	6.5	0.18
	0% starch/PBS	−0.368	12.8	0.28
	70% starch/PCL	−0.031	0.5	0.01
Effect of aging	0.5 days	−0.102	1.3	0.03
	7 days	−0.528	6.8	0.19
	27 days	0.283	7.1	0.17
	57 days	−0.067	1.1	0.03

non-dimensional stress decreased with increasing starch content. This could be due to the higher viscosity and hence lower injection speed with increasing starch content. As shown by Isayev and Crouthamel [10], increasing the melt temperature (and hence reducing the viscosity) or the injection rate leads to the predominance of thermal stresses over flow stresses, resulting in higher surface compressive stresses. Thus, in blends with lower starch content which have a lower viscosity, the effect of tensile flow stresses is negligible, leading to the higher non-dimensional stress. Or conversely, the higher viscosity of blends with increasing starch content leads to a greater influence of tensile flow stresses, thus, decreasing the non-dimensional surface compressive stresses. Another influence could be that increasing starch content decreases the thermal conductivity of the blend, thus reducing the cooling rate. This would let the stresses relax relatively more in blends with higher starch content. Hence, the starch in the blend is probably behaving like a filler material.

Average stress per unit width over half the specimen thickness, as estimated by Eq. (3), is reported in Table 8. Except for one case where this magnitude was about 13% of the maximum stress, all the others were found to be less than 10% of the maximum stress value. This is well within the 10–20% range reported by Isayev and Crouthamel [10] for the layer removal technique. This value is associated with the error inherent in the technique due to measurement and mathematical errors in the lengthy procedure. No correlation was observed between the variation in average stress values and molding conditions or starch content. This suggests that the average stress measured by the stress relaxation methods of Li [17] and Kubat and Rigdahl [18] are quite different from this estimation. Investigations by Bhattacharya [19] showed that the average residual stress obtained by the Li method was negative and increased in magnitude as starch content was increased from 0 to 60%. This trend is in qualitative agreement with the results obtained in the current study.

Table 8 also shows the deviation of the stress distribution curves from equilibrium expressed in terms of the non-dimensional parameter of Eq. (4). The values vary from 0.01 to 0.28. This variation follows the same trend as the average stress expressed as a percentage of the maximum stress except for one case in the aging experiments.

3.2.6. Comparison of different polyesters

The effect of using PCL 767 as the synthetic polymer component in a blend containing 70% starch is shown in Fig. 8. Maximum compressive and tensile stress magnitudes were found to be about 7 times lower for the blend containing PCL 767. This may be explained by the substantially large difference of about 60°C between the melt temperature and the solidification point of PCL 767, which allowed a longer duration for stresses to relax. The smaller difference between mold wall temperature and melt temperature, about 100°C, also contributed to this effect by decreasing the cooling rate. For the PBS blends, the difference between melt temperature and the solidification point of the synthetic component was only about 30°C. And the difference between melt temperature and mold wall temperature was about 125°C.

3.3. Density gradient

The effect of molding conditions on the density distribution across the part thickness is shown in Fig. 10. Overall, all the samples show a higher density at the interior with a slight decrease towards the surface and a steep drop close

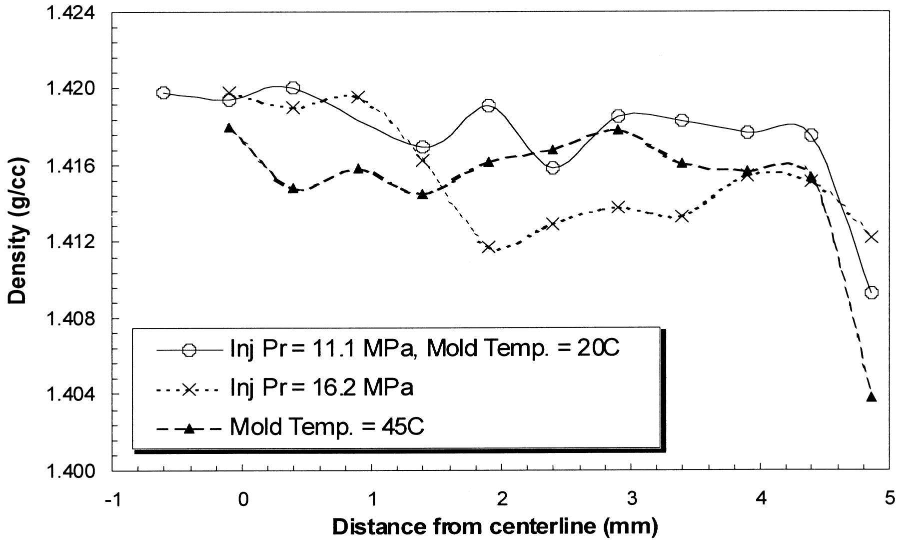

Fig. 10. Effect of injection pressure and mold temperature on the density distribution for B70.

to the surface. This profile is similar to the trend found in semi-crystalline polymers as reported in previous studies [20,21]. Thus, for a blend containing 70% starch, the crystallinity of the 30% synthetic polymer content appears to dominate over the effect of the residual stress distribution, though the observed results could be due to a combination of both. The steep drop in density at the surface indicates that the synthetic polymer phase in this layer may remain amorphous due to high cooling rates. The presence of a steep gradient close to the surface is similar to results observed by Isayev and Hariharan [22]. The average densities obtained for the samples molded under the different conditions are shown in Table 9.

The effect of injection pressure is shown in Fig. 10. The average densities of both samples were the same (Table 9). The density close to the center was also the same at both injection pressures. But the density at 1.5–4.5 mm from the center is lower at an injection pressure of 160 bar, while the surface density is higher. This could happen due to shear heating produced by the higher injection rates associated with a higher injection pressure. Since the shear rate is at its maximum close to the cavity wall, a higher temperature rise would occur at the skin layer, leading to greater crystallinity due to slower cooling and hence a higher density compared to the sample molded at 11.1 MPa. But the higher temperatures in the layers a little more to the interior would imply a lower density of the melt itself due to thermal expansion. Thus, a lesser quantity of material is packed in that region leading to a lower density. The density in the center region remains the same at either injection pressure, as there is negligible shear heating and maximum packing there. Isayev and Hariharan [22] found a negligible influence of the melt flow rate on the density distribution.

Table 9
Average density values obtained for B70 molded under different conditions. The parameter values were varied one at a time, with all other parameter values remaining the same as under reference conditions

Molding conditions	Average density (g/cm^3)
Reference	1.4198
Injection pressure 11.1 MPa	
Packing pressure 11.1 MPa	
Packing time 20 s	
Mold temperature 20°C	
Nozzle temperature 155°C	
Injection pressure 16.2 MPa	1.4199
Packing pressure 6.1 MPa	1.4181
Packing time 5 s	1.4205
Mold temperature 45°C	1.4143
Nozzle temperature 155°C	1.4183

Increasing the mold temperature to 45°C from 20°C caused a reduction in density as exhibited both by the density distribution (Fig. 10) and the average density (Table 9). The average density decreased by a substantial 0.384%. In fact, mold temperature had the largest influence on the average density among all parameters compared. This is in contradiction to the fact that a higher mold temperature would lead to lower cooling rates and hence higher crystallinity in the synthetic polymer, increasing its density. The results of Greener and Kenyon [23] and Isayev and Hariharan [22] also indicate the final quenching temperature has a significant influence on the density.

There does not appear to be any significant effect of packing pressure, packing time, and barrel/nozzle temperature on the density distribution for the range considered. The average density was 0.122% lower for the lower packing pressure (Table 9). This is expected, as a lower packing pressure would reduce the amount of melt packed into the cavity after filling. The results of Isayev and Hariharan [22] indicate that the gapwise averaged density was the same for packing pressures of 1.4 and 3.5 MPa while it increased significantly when the packing pressure was raised to

1000 psi. The surface density for a packing time of 5 s was 1.397 g/cc while it was 1.409 g/cc for a packing time of 20 s, a 0.85% difference. There was no effect on the average density (Table 9) indicating that at 5 s after filling, the packing pressure does not have a significant impact on density.

Increasing the barrel nozzle temperature by 10°C, and thereby raising the melt temperature, does not have a clearly distinguishable effect on the density distribution. The influence of increasing the melt temperature is not expected to be significant as crystallization occurs only below the freezing point of the melt and the cooling rate remains the same as the surrounding mold temperature is constant. This is in agreement to the observations of Moy and Kamal [20] who found melt temperature to have a negligible effect. This is also reflected in the studies by Greener and Kenyon [23] and Isayev and Hariharan [22], where the initial temperature of quenching experiments had no influence on the density distribution.

4. Conclusions

The residual stress profiles in starch/synthetic polymer blends was determined to be parabolic in nature with compressive stresses at the surface and tensile stresses towards the center. This indicates that thermal stresses dominate over flow stresses for the part dimensions and molding conditions considered in this study. The maximum surface compressive stress reached up to 25% of the UTS and was typically 1.85–2.5 times the maximum tensile stress. The main factors influencing the magnitude of residual stress in starch synthetic polymer blends were found to be injection pressure, packing pressure, mold temperature, aging and starch content. Increasing the injection pressure and mold temperature led to a decrease in the magnitude of the interior tensile stresses. Decreasing the packing pressure caused a decrease in the magnitude of both compressive and tensile stresses. Annealing reduced the stresses to extremely small values. The magnitude of stresses decreased with aging due to relaxation. Increasing the starch content from 0 to 70% was found to cause almost a four-fold increase in the magnitude of residual stresses. A non-dimensional stress analysis showed this to be not only due to the increase in Young's modulus and Poisson's ratio values but also due to the influence on the flow characteristics of the blends. Use of PCL-767 as the synthetic polymer component led to a reduction in the residual stress magnitude, mainly due to the lower mechanical strength of the synthetic polymer and longer cooling time due to its lower crystallizing temperature.

The error in the residual stress measurement was estimated by the ratio of the average stress to the maximum stress. This was found to be a maximum of 12%, which was well within the range of experimental errors reported in the literature. Thus, the use of an abrasive water-jet can be said to be suitable for the process.

Several mechanical properties were determined for the starch/synthetic polymer blends. A measurement of the UTS for samples molded under the various experimental conditions showed a negligible variation. Brief exposure to water was also found to have a negligible effect. The Young's modulus and Poisson's ratio increased substantially with increasing starch content, but the UTS did not exhibit a very marked rise.

Density measurements across the part thickness showed the presence of a steep gradient close to the surface with a relatively flat distribution in the interior. The density in the interior was higher than at the surface, which is consistent with reports in the literature for semi-crystalline polymers. This indicates the dominance of the synthetic component in the blends with regard to density distribution. Varying molding conditions seem to have a rather complex effect on the average density and density distribution. All of these effects could not be explained by a conventional understanding of the injection molding process, indicating the complex nature of starch/synthetic polymer blends.

Thus, it was generally observed that the influence of molding conditions on the residual stress distribution is similar to that found in other polymers. The maximum magnitude of stresses measured was about 25% of the break strength, which is quite high, though it may partly be explained by the large thickness of the specimens used in this study. The presence of compressive surface stresses can be used to advantage by reducing the incidence of cracks and raising the yield/break strength. For the range of molding conditions studied, the surface stresses were never found to be tensile in nature and thus do not seem to be a cause for concern.

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